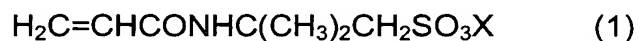


Process For The Preparation Of Stable Polymer Concentrates

- [0001] The present invention relates to a process for the preparation of concentrates from copolymers based on acryloyldimethyltauric acid or salts thereof.
- [0002] The polymers based on acryloyldimethyltauric acid or salts thereof described in EP 816 403, which are preferably prepared by precipitation polymerization, cover broad application properties and can be used as thickener, consistency-imparting agent, emulsifier, dispersant, slip-agent, conditioner and/or stabilizer in cosmetic, dermatological and pharmaceutical compositions.
- [0003] The copolymers based on acryloyldimethyltauric acid or salts thereof preferably prepared by precipitation polymerization and corresponding to the prior art are pulverulent substances with application disadvantages resulting therefrom. Pulverulent substances, in principle, hold the risk of dust explosion, and in addition the storage stability of the powders is adversely affected as a result of hygroscopicity.
- [0004] For the processing and/or use of the pulverulent products, the dissolution operation (the polymers are preferably incorporated into aqueous media) is in most cases very time-consuming. The dissolution operation of the pulverulent products can, depending on the size of the batch, take an hour or more. In addition, incomplete dissolution/swelling of the pulverulent products is often observed, which leads to a reduction in the quality and stability of the end formulation (formation of lumps). In addition, the processing and/or use of the pulverulent products requires particular stirring and dispersion devices in order to dissolve, or to suspend, respectively, the polymers based on acryloyldimethyltauric acid or salts thereof.

- [0005] The object of the present invention was to develop a process for the preparation of polymer concentrates comprising polymers based on acryloyldimethyltauric acid or salts thereof. The polymer concentrates should, when present in highly concentrated liquid or liquid-disperse form, i.e. when the highest possible polymer content arises, have a low viscosity combined with high stability of the solution or dispersion.
- [0006] Surprisingly, it has been found that storage-stable and thermostable concentrates in liquid or liquid-disperse form of copolymers described below comprising acryloyldimethyltauric acid or salts thereof can be prepared if a solvent or solvent mixture is added after the polymerization reaction whose boiling point is higher than the boiling point of the polymerization media, solvent or solvent mixture used for the polymerization, and then removing the lower-boiling polymerization medium, solvent or solvent mixture, optionally at a pressure which is lowered relative to atmospheric pressure, and optionally at a temperature which is increased relative to room temperature (25°C).
- [0007] The invention provides a process for the preparation of concentrates in liquid or liquid-disperse form comprising
- [0008] 5 to 80% by weight, preferably 10 to 80% by weight, particularly preferably 20 to 60% by weight, especially preferably 30 to 40% by weight, of a polymer which, in random distribution, has come, in an amount of 90 to 99.99% by weight, from monomers of the formula (1)



in which X is a cation or a mixture of cations, and X consists of not more than 10 mol% of protons, and,

in an amount of 0.01 to 10% by weight, from monomers with at least two olefinic double bonds,

II) 20 to 95% by weight, preferably 20 to 90% by weight, particularly preferably 40 to 80% by weight, especially preferably 60 to 70% by weight, of one or more emulsifiers and/or a solvent or solvent mixture, and

III) 0 to 30% by weight, preferably 0 to 10% by weight, particularly preferably 0 to 5% by weight, of water,

wherein the concentrate is prepared by

a) free-radical polymerization of the monomers of formula (1) in the presence of the monomers having at least two olefinic double bonds, preferably by solution polymerization, gel polymerization, by an emulsion process, precipitation process, high-pressure process or suspension process in a polymerization medium which behaves largely inertly with regard to free-radical polymerization reactions and permits the formation of high molecular weights, preferably water and lower, tertiary alcohols or hydrocarbons having 3 to 30 carbon atoms, particularly preferably tertbutanol,

b) addition of a higher-boiling solvent or solvent mixture and/or one or more emulsifiers and optionally water to the mixture of polymer and polymerization medium, where the boiling point of the higher-boiling solvent or solvent mixture is at least 10°C higher than that of the polymerization medium used for the polymerization and

c) removal of the lower-boiling polymerization medium, optionally at a pressure which is lowered relative to atmospheric pressure, and

optionally at a temperature which is increased relative to room temperature.

- [0009] Preferably, the concentrates prepared according to the process of the invention comprise polymers comprising 98 to 99.5% by weight of units which have come from monomers of the formula (1) and 0.5 to 2% by weight of crosslinking structures which have come from monomers with at least two olefinic double bonds.
- [00010] The counterion X in the formula (1) is, in particular, a proton, a cation of an alkali metal, an equivalent of a cation of an alkaline earth metal or is an ammonium ion.
- [00011] Particularly preferred polymers are notable for the fact that 90 to 100 mol% of the cations X consist of ammonium ions and 0 to 10 mol% of protons.
- [00012] The monomers with at least two olefinic double bonds are preferably chosen from dipropyl glycol diallyl ether, polyglycol diallyl ether, triethylene glycol divinyl ether, hydroquinone diallyl ether, tetraallyloxyethane or other allyl or vinyl ethers of multifunctional alcohols, tetraethylene glycol diacrylate, triallylamine, trimethylolpropane diallyl ether, methylene bisacrylamide, divinylbenzene or trimethylolpropyl tri(meth)acrylate. The monomers with at least two olefinic double bonds lead to crosslinking structures during the polymerization.
- [00013] The concentrates prepared by the process according to the invention comprise polymers prepared by free-radical polymerization of 90-99.99% by weight of the compounds of the formula (1) and 0.01-10% by

weight of one or more crosslinkers which contain at least two olefinic double bonds.

[00014] Preferably, these polymers are prepared by

- a) dissolution or dispersion of the compounds of the formula (1) in a solvent or solvent mixture, where X can in this case also consist of up to 100 mol% of protons;
- b) optional neutralization of the resulting solution or dispersion by means of one or more bases so that at least 90 mol% of the sulfonic acid groups are converted to the salt form,
- c) addition of one or more crosslinkers with at least two olefinic double bonds to the solution or dispersion obtained as in a) and b) and
- d) starting of the polymerization in a manner known per se, e.g. by means of free-radical-forming compounds, at a temperature of from 10 to 150°C, the solvent or solvent mixture mentioned in a) being chosen such that the resulting polymers are largely insoluble in the solvent or solvent mixture.

[00015] In a preferred embodiment, the polymerization is carried out as a precipitation polymerization.

[00016] In detail, the described polymers can be prepared by precipitation polymerization as follows. The reaction medium used is preferably a water-soluble alcohol or a mixture of two or more water-soluble alcohols having 1 to 4 carbon atoms, preferably tert-butanol, where the water content of the alcohol or alcohol mixture must not exceed 10% by weight. The type and amount of solvent has to be chosen such that the

amount of 2-acrylamido-2-methylpropanesulfonic acid and/or salts thereof used is largely soluble or dispersible. Largely soluble or dispersible is understood as meaning that, even after scraping the stirrer, no solid material settles out of the solution or dispersion. By contrast, the polymer which forms in the course of the reaction should, however, be largely insoluble in the chosen solvent (or solvent mixture). Largely insoluble is understood here as meaning that, in the course of the polymerization, a readily stirrable pasty polymer mass forms in which no lumps or agglutinations must form. The filtrate obtainable by filtering the paste with suction should have a solids content of at most 5% by weight. If the polymers are soluble in the chosen solvent or solvent mixture to a greater degree, clumping may arise during the drying of the polymer paste.

- [00017] The polymerization reaction itself is triggered in a manner known per se, e.g. by free-radical-forming compounds, such as azoic initiators (e.g. azobisisobutyronitrile), peroxides (e.g. dilauryl peroxide) or persulfates, in a suitable temperature interval from 20 to 120°C, preferably between 40 and 80°C, and is continued over a period of 30 minutes to several hours.
- [00018] Besides the polymer, the polymer concentrates prepared by the process according to the invention also comprise one or more emulsifiers and/or a solvent or solvent mixture in the stated amount. If emulsifiers are used as the sole component II), the proportion of the solvent or solvent mixture is thus 0% and, accordingly, the proportion of the emulsifiers is 0% when the component II) consists only of a solvent or solvent mixture. Preference is given to using a mixture of emulsifier and solvent or solvent mixture as second component.

[00019] Suitable emulsifiers are addition products of from 0 to 30 mol of alkylene oxide, in particular ethylene oxide, propylene oxide, butylene oxide, onto linear fatty alcohols having 8 to 22 carbon atoms, onto fatty acids having 12 to 22 carbon atoms, onto alkylphenols having 8 to 15 carbon atoms in the alkyl group and onto sorbitan esters; (C₁₂-C₁₈)-fatty acid mono- and diesters of addition products of from 0 to 30 mol of ethylene oxide onto glycerol; glycerol mono- and diesters and sorbitan mono- and diesters of saturated and unsaturated fatty acids having 6 to 22 carbon atoms and optionally the ethylene oxide addition products thereof; addition products of from 15 to 60 mol of ethylene oxide onto castor oil and/or hydrogenated castor oil; polyol and, in particular, polyglycerol esters, such as, for example, polyglycerol polyricinoleate and polyglycerol poly-12-hydroxystearate. Preference is given to liquid fatty acid esters which may either be ethoxylated (PEG-10 polyglyceryl-2 laurate) or nonethoxylated (polyglyceryl-2 sesquiosostearate).

[00020] Further dispersion concentrates prepared by the process of the invention preferably comprise sorbitol esters prepared by reacting sorbitol with fatty acid methyl esters or fatty acid triglycerides. The fatty acid radical in the fatty acid methyl esters and fatty acid triglycerides generally contains 8 to 22 carbon atoms and can be straight-chain or branched, saturated or unsaturated. Examples of these are palmitic acid, stearic acid, lauric acid, linoleic acid, linolenic acid, isostearic acid or oleic acid. Suitable fatty acid triglycerides are all natural animal or vegetable oils, fats and waxes, for example olive oil, rapeseed oil, palm kernel oil, sunflower oil, coconut oil, linseed oil, castor oil, soybean oil, optionally also in refined or hydrogenated form. Since these natural fats, oils and waxes are normally mixtures of fatty acids of varying chain length, this also applies to the fatty acid radicals in the sorbitol esters used according to the invention. The sorbitol esters used according to the invention can also be alkoxylated, preferably ethoxylated.

- [00021] In addition, it is possible to use anionic emulsifiers, such as ethoxylated and nonethoxylated mono-, di- or triphosphoric esters, but also cationic emulsifiers, such as mono-, di- and trialkyl quats and their polymeric derivatives.
- [00022] Likewise suitable are mixtures of compounds from two or more of these classes of substances.
- [00023] As well as the polymer based on acryloyldimethyltauric acid or salts thereof, the concentrates prepared by the process according to the invention can comprise one or more solvents, preferably from the group of hydrocarbons, ester oils, vegetable oils and silicone oils.
- [00024] The solvents used according to the invention include oils, such as hydrocarbon oils with linear or branched, saturated or unsaturated C₇-C₄₀-carbon chains, for example vaseline, dodecane, isododecane, cholesterol, lanolin, hydrogenated polyisobutylenes, docosanes, hexadecane, isohexadecane, paraffins and isoparaffins;
- [00025] oils of vegetable origin, in particular liquid triglycerides, such as sunflower oil, corn oil, soybean oil, rice oil, jojoba oil, babusscu oil, pumpkin oil, grapeseed oil, sesame oil, walnut oil, apricot oil, macadamia oil, avocado oil, sweet almond oil, lady's smock oil, castor oil, olive oil, peanut oil, rapeseed oil and coconut oil;
oils of animal origin, preferably beef tallow, perhydrosqualene, lanolin;
synthetic oils, such as purcellin oil, linear and/or branched fatty alcohols and fatty acid esters, preferably Guerbet alcohols having 6 to 18, preferably 8 to 10, carbon atoms; esters of linear (C₆-C₁₃)-fatty acids with linear (C₆-C₂₀)-fatty alcohols; esters of branched (C₆-C₁₃)-carboxylic acids with linear (C₆-C₂₀)-fatty alcohols, esters of linear (C₆-

C₁₈)-fatty acids with branched alcohols, in particular 2-ethylhexanol; esters of linear and/or branched fatty acids with polyhydric alcohols (such as, for example, dimerdiol or trimerdiol) and/or Guerbet alcohols; alcohol esters of C₁-C₁₀-carboxylic acids or C₂-C₃₀-dicarboxylic acids, C₁-C₃₀-carboxylic monoesters and polyesters of sugars, C₁-C₃₀-monoesters and polyesters of glycerol; waxes, such as beeswax, paraffin wax or microwaxes, optionally in combination with hydrophilic waxes, such as, for example, cetylstearyl alcohol; fluorinated and perfluorinated oils; monoglycerides of C₁-C₃₀-carboxylic acids, diglycerides of C₁-C₃₀-carboxylic acids, triglycerides of C₁-C₃₀-carboxylic acids, for example triglycerides of caprylic/capric acids, ethylene glycol monoesters of C₁-C₃₀-carboxylic acids, ethylene glycol diesters of C₁-C₃₀-carboxylic acids, propylene glycol monoesters of C₁-C₃₀-carboxylic acids, propylene glycol diesters of C₁-C₃₀-carboxylic acids, and also propoxylated and ethoxylated derivatives of the abovementioned classes of compounds.

[00026] Suitable silicone oils are dimethylpolysiloxanes, cyclomethicones, polydialkylsiloxanes $R_3SiO(R_2SiO)_xSiR_3$, in which R is methyl or ethyl, particularly preferably methyl, and x is a number from 2 to 500, for example the dimethicones available under the trade names VICASIL (General Electric Company), DOW CORNING 200, DOW CORNING 225, DOW CORNING 200 (Dow Corning Corporation); trimethylsiloxysilicates $[(CH_2)_3SiO]_{1/2}x[SiO_2]_y$, where x is a number from 1 to 500 and y is a number from 1 to 500; dimethiconols $R_3SiO[R_2SiO]_xSiR_2OH$ and $HOR_2SiO[R_2SiO]_xSiR_2OH$, where R is methyl or ethyl and x is a number up to 500, polyalkylarylsiloxanes, for example the polymethylphenylsiloxanes available under the trade names SF 1075 METHYLPHENYL FLUID (General Electric Company) and 556 COSMETIC TRADE PHENYL TRIMETHICONE FLUID (Dow Corning Corporation), polydiarylsiloxanes, silicone resins, cyclic

silicones and amino-, fatty acid-, alcohol-, polyether-, epoxy-, fluorine- and/or alkyl-modified silicone compounds, and also polyether siloxane copolymers, as described in US 5,104,645 and the specifications cited therein, which, at room temperature, may be in liquid form or in resin form.

- [00027] In a preferred embodiment, the concentrates prepared by the process according to the invention consist of dispersions of the polymers in a liquid matrix comprising oil, emulsifier, dispersant and/or water. Preference is also given here to liquid-disperse forms with the highest possible polymer content and low viscosity coupled with high stability of the dispersion. In the concentrates according to the invention, preference is given to using oils, emulsifiers and dispersants which are acceptable in cosmetic, pharmaceutical and dermatological formulations.
- [00028] The invention further also provides the concentrates obtainable by the process according to the invention.
- [00029] The concentrates according to the invention are suitable as thickener, consistency-imparting agent, emulsifier, solubilizer, dispersant, slip agent, adhesive, conditioner and/or stabilizer in an excellent manner for the formulation of cosmetic, pharmaceutical and dermatological compositions, in particular of oil-in-water emulsions in the form of creams, lotions, cleansing milk, cream gels, spray emulsions, e.g. body lotions, after sun lotions, sun screen compositions and deodorant sprays.
- [00030] The invention further also provides cosmetic, pharmaceutical and dermatological preparations comprising a concentrate according to the invention.

- [00031] The polymer concentrates according to the invention are used in the cosmetic, pharmaceutical and dermatological preparations in amounts by weight of from 0.01 to 10% by weight, preferably 0.1 to 5% by weight, particularly preferably 0.5 to 3% by weight, based on the finished compositions.
- [00032] The cosmetic, pharmaceutical and dermatological preparations may comprise anionic, cationic, nonionic, zwitterionic and/or amphoteric surfactants, and also further auxiliaries and additives, cationic polymers, film formers, superfatting agents, stabilizers, biogenic active ingredients, glycerol, preservatives, pearlizing agents, dyes and fragrances, solvents, opacifiers, and also protein derivatives, such as gelatin, collagen hydrolysates, natural and synthetic-based polypeptides, egg yolk, lecithin, lanolin and lanolin derivatives, fatty alcohols, silicones, deodorizing agents, substances with a keratolytic and keratoplastic action, enzymes and carrier substances. Furthermore, antimicrobially active agents can be added to the compositions according to the invention.
- [00033] In addition, the cosmetic, pharmaceutical and dermatological preparations can comprise organic solvents. In principle, suitable organic solvents are all mono- or polyhydric alcohols. Preference is given to using alcohols having 1 to 4 carbon atoms, such as ethanol, propanol, isopropanol, n-butanol, isobutanol, tert-butanol, glycerol and mixtures of said alcohols. Further preferred alcohols are polyethylene glycols with a relative molecular mass below 2000. In particular, a use of polyethylene glycol with a relative molecular mass between 200 and 600 and in amounts up to 45% by weight and of polyethylene glycol with a relative molecular mass between 400 and 600 in amounts of from 5 to 25% by weight is preferred. Further suitable solvents are, for example,

triacetin (glycerol triacetate) and 1-methoxy-2-propanol. Short-chain anionic surfactants, in particular arylsulfonates, for example cumene- or toluenesulfonate, have a hydrotropic effect.

- [00034] The following examples of concentrates containing polymers based on acryloyldimethyltauric acid or salts thereof are intended to illustrate the subject-matter of the invention in more detail without limiting it thereto. The percentages given are % by weight.
- [00035] Example A (from table) (high emulsifier concentration)
- [00036] 500 g of tert-butanol and 80 g of acryloyldimethyltauric acid are initially introduced into a 1 liter flat-flange flask with temperature sensor, reflux condenser, precision-ground glass stirrer and pH control. The mixture is then neutralized by introducing gaseous ammonia, and 1.9 g of trimethylolpropane triacrylate (crosslinker) are added to the reaction mixture. The reaction mixture is then rendered inert by introducing N₂, heated to 60°C and the reaction is started after 30 minutes by adding 1.2 g of dilauroyl peroxide. An exothermic reaction results in which the internal temperature increases by several degrees. After about 10 minutes, the resulting polymer precipitates out, which is evident from a steady increase in the solution viscosity. At the end of the exothermic phase (about 20-30 minutes), the reaction mixture is heated to the boiling temperature and after-boiled for 2 hours to complete the reaction. During this time, the viscosity of the solution decreases again. Afterwards, the reflux condenser is replaced by a distillation bridge. Then, 45 g of Hostaphat KL 340D, 75 g of Emulsogen SRO, 20 g of mineral oil (low viscosity) and 25 g of isopropyl palmitate are added to the polymer suspension, and the major part of the tert-butanol is then removed by distillation with stirring. By applying a vacuum, the tert-butanol residues are removed from the mixture. It must be ensured that

although the applied vacuum permits the removal of the tert-butanol by distillation, it does not exceed the corresponding boiling temperature of the solvent at this pressure. After the tert-butanol has been separated off, the mixture is cooled and the product is removed from the flask.

[00037] Example C (from table) (low emulsifier concentration)

[00038] 400 g of tert-butyl and 80 g of acryloyldimethyltauric acid are initially introduced into a 1 liter flat-flange flask with temperature sensor, reflux condenser, precision-ground glass stirrer and pH control. The mixture is then neutralized by introducing gaseous ammonia, and 1.65 g of TMPTA (trimethylolpropane triacrylate) are added to the reaction mixture. The reaction mixture is then rendered inert by introducing N₂, heated to 60°C and the reaction is started after 30 minutes by adding 1.5 g of dilauroyl peroxide. An exothermic reaction results in which the internal temperature increases by several degrees. After about 10 minutes, the resulting polymer precipitates out, which is evident from a steady increase in the solution viscosity. At the end of the exothermic phase (about 20-30 minutes), the reaction mixture is heated to the boiling temperature and after-boiled for 2 hours to complete the reaction. During this time, the viscosity of the solution decreases again. Afterwards, the reflux condenser is replaced by a distillation bridge. Then, 6 g of Hostacerin DGI, 4 g of Hostaphat KL 340D, 55 g of mineral oil (low viscosity) and 55 g of isopropyl palmitate are added to the polymer suspension, and the major part of the tert-butanol is then removed by distillation with stirring. By applying a vacuum, the tert-butanol residues are removed from the mixture. It must be ensured that although the applied vacuum permits the removal of the tert-butanol by distillation, it does not exceed the corresponding boiling temperature of the solvent at this pressure. After the tert-butanol has been separated off, the mixture is cooled and the product is removed from the flask.

[00039] Various basic formulations with different emulsifier and oil concentrations were prepared. The resulting polymer concentrates were assessed according to appearance, viscosity and stability (sedimentation upon storage at 25°C for 3 weeks). Table 1 shows examples of concentrates which are flowable and storage-stable.

Table 1

Dispersion concentrate	A	B	C	D
Polymer	32	36	40	30
Hostacerin DGI	-	30	3	51
Hostaphat KL 340 D	18	18	2	13
Emulsogen SRO	30	-	-	-
Mineral oil, low-viscosity	10	-	27.5	6
Isopropyl palmitate	10	-	27.5	-
Myritol 318	-	16	-	-

[00040] The figures given in table 1 are % by weight. The dispersion concentrates B and D were prepared analogously to A, but varying the emulsifiers and oils.

Hostacerin DGI	Polyglyceryl-2 Sesquiosostearate
Hostaphat KL 340 D	Trilaureth-4 Phosphate
Emulsogen SRO	Rapeseed Oil Sorbitol Esters
Myritol 318	Caprylic/Capric Triglyceride

[00041] Examples of cosmetic preparations based on the concentrates according to the invention. The percentages are % by weight.

Example 1: Moisturizing lotion

A	Almond oil	7.00%
	Cyclomethicones	5.00%
B	Dispersion concentrate A	4.00%
C	Glycerol	7.00%
	Water	ad 100%
	Preservative	q.s.
D	Fragrance	0.30%

Preparation

- I Mix A and B.
- II Stir solution of C into I.
- III Add D to II.
- IV Homogenize
- V pH 5.5

Example 2: Sunscreen lotion

A	Vaseline	5.00%
	Paraffin oil	10.00%
	Dispersion concentrate B	2.00%
	Tocopheryl acetate	1.00%
	Octyl methoxycinnamate	2.00%
	Parasol 1789	0.20%
B	Ethanol	10.00%
C	Butylene glycol	5.00%
	Water	ad 100%

[00042] Preparation

- I A and C are heated separately to 75°C, then combined and cooled with stirring to 65°C, homogenized and cooled further to 35°C,
- II B is stirred into I, it is homogenized and cooled to room temperature

Example 3: O/W skin milk

A	Isopropyl palmitate	4.00%
	Almond oil 5.00%	4.00%
	Wheatgerm oil	1.00%
	Cetearyl isononanoate	8.00%
	®Cetiol SN (Henkel)	
B	Dispersion concentrate C	1.50%
C	Water	ad 100%
D	Fragrances	0.30%

[00043] Preparation

- I Add B to A with stirring
- II Stir C and D into I
- III Homogenize emulsion